Silver-catalyzed hydrosilylation of aldehydes†

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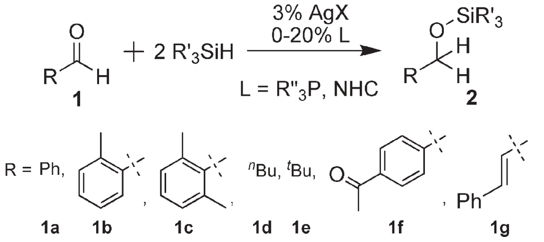
Silver triflate, either alone or in the presence of an appropriate phosphine or NHC ligand, has been shown to catalyze the chemoselective hydrosilylation of aromatic and aliphatic aldehydes to yield silyl ethers, thus representing the first systematic application of silver species as catalysts for the hydrosilylation of unsaturated organic substrates.

The metal-catalyzed hydrosilylation of carbonyl compounds is an atom-economical methodology that provides direct access to synthetically useful O-protected silyl alcohols.[1] In addition to the diversity of main group and transition metal catalysts for carbonyl hydrosilylation that have been identified over the past three decades,[1,2] including those based on Ti,[2b] Ru,[2c] and Rh,[2d,e] effective group 11 catalysts have also emerged. The groups of Stryker,[3] Lipshutz,[4] Nolan,[5] and others have demonstrated that Cu complexes featuring either phosphine or *N*-heterocyclic carbene (NHC) ligands can function as active and selective catalysts for carbonyl hydrosilylations, while a single report by Hosomi and co-workers highlights the catalytic utility of Au species for such transformations.[6] In contrast, reports focused on the application of Ag species as hydrosilylation catalysts are absent from the literature. Indeed, Ag salts are often viewed as being catalytically inactive in hydrosilylation chemistry, and in this context are commonly employed as innocent anion exchange agents for the *in situ* generation of cationic transition (and other) metal catalysts.[7]

Inspired by recent reports from the groups of He[8] and Li[9] in which Ag complexes have been shown to mediate the addition of σ-bonds to unsaturated organic molecules, we became interested in evaluating the catalytic utility of Ag species in carbonyl hydrosilylations, including examining the influence of supporting ligands on such Ag-mediated transformations. Herein we report the Ag-catalyzed chemoselective addition of silanes to aldehydes, which to the best of our knowledge represents the first systematic application of Ag species as catalysts for the hydrosilylation of unsaturated organic compounds.

The hydrosilylation of benzaldehyde (**1a**) with Me_2PhSiH to give the silyl ether **2a** was selected as a preliminary test reaction for Ag-mediated carbonyl hydrosilylations (Scheme 1). While reactions conducted in THF at 24 °C employing 3 mol% $AgSbF_6$ generated the benzaldehyde trimer (**3a**) in 97% yield after 15 min, under analogous conditions employing 3 mol% AgOTf, **2a** was obtained in 94% yield, along with only 6% of **3a** (Table 1, entry 1). Similar results were obtained for reactions conducted at 70 °C using 3 mol% AgOTf in THF. Although the initial and overall reaction rates were lowered considerably upon the addition of 20 mol% Et_3P to 3 mol% AgOTf, the use of this catalyst mixture in THF enabled the clean formation of **2a** in 98% yield after 24 h at 70 °C, in the absence of **3a** or other by-products (entry 2).[10a,b] While excellent yields of **2a** were also obtained in toluene or DMSO, 1,2-dichloroethane proved to be a less effective solvent. By comparison, reactions employing 3 mol% Me_3SiOTf at 70 °C in THF afforded **3a** quantitatively, and no reaction was observed when a Et_3P–Me_3SiOTf catalyst system was used at 70 °C in THF.



Scheme 1 Silver-catalyzed addition of silanes to aldehydes.

The conversion of **1a** to **2a** mediated by Et_3P–AgX mixtures in THF was found to vary based on the counteranion employed, with catalysts derived from AgCl (57%) proving inferior to those based on AgOTf (98%), $AgBF_4$ (93%), or $AgSbF_6$ (95%). However, the observation that a R_3P–AgCl mixture is capable

Table 1 Addition of Me_2PhSiH to aldehydes[a]

Entry	Aldehyde	% Et_3P	% **2**[b]	% **3**[b,c]	% other[b]	TOF[d]
1	**1a**	0	94	6	<1	133
2	**1a**	20	98	<1	<1	29
3	**1b**	0	88	<1	2	121
4	**1b**	20	94	<1	1	49
5	**1c**	0	50	<1	40	121
6	**1c**	20	76	<1	1	<1
7	**1d**	0	9	58	20	117
8	**1d**	20	86	1	12	1
9	**1e**	0	7	<1	1	11
10	**1e**	20	48	<1	6	1
11	**1f**	0	62	<1	24	114
12	**1f**	20	>99	<1	<1	37
13	**1g**	0	48	<1	17	87
14	**1g**	20	99	<1	1	37

[a] Reactions in THF with 2 equiv. Me_2PhSiH and 3 mol% AgOTf versus **1**. In the absence of Et_3P, the addition of silane resulted in rapid change of the solution color from colorless to yellow, followed by the immediate precipitation of Ag(s). [b] Yields quoted with respect to **1** consumed (after 24 h at 70 °C for 20% Et_3P, or 0.25 h at 24 °C for 0% Et_3P) based on GC-MS and GC-FID data (average of two runs). [c] Aldehyde trimer. [d] Turnover frequency (TOF, h^{-1}) at 0.25 h, based on the consumption of **1**.

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of mediating such transformations is noteworthy, given that AgCl elimination in the presence of excess phosphine is often exploited during the *in situ* preparation of cationic metal catalysts for carbonyl hydrosilylations. For convenience, AgOTf was used in THF for all subsequent catalytic investigations.

Intrigued by these preliminary catalytic results, we became interested in assessing the impact of employing alternative ligands in Ag-mediated hydrosilylations. Given the exceptional selectivity exhibited by the catalyst system derived from a combination of excess Et_3P relative to AgOTf (20 : 3), we anticipated that the structurally related bidentate ligand 1,2-bis(diethylphosphino)ethane (DEPE) might give rise to an even more effective catalyst system. To our surprise, catalysts derived from the combination of either 10 or 20 mol% DEPE with 3 mol% AgOTf afforded significantly lower yields of **2a** (45% and 68%) than were obtained in analogous reactions employing 20 mol% Et_3P (98%). Although we are hesitant to draw detailed mechanistic conclusions from such an observation, it is possible that the DEPE ligands may serve to bridge rather than chelate in this system, thereby generating what may be catalytically less-competent oligomeric structures.[11] In returning our focus to monophosphines, the use of 20 mol% ^{n}Bu$_3$P afforded an Ag-catalyst system that provided cleanly a yield of **2a** (95%) comparable to that obtained by use of 20 mol% Et_3P. In contrast, the combination of 3 mol% AgOTf and 20 mol% of one of the more sterically hindered branched trialkylphosphines Cy_3P, ^{i}Pr$_3$P, or ^{t}Bu$_3$P, or the triarylphosphine Ph_3P, afforded significantly lower yields of **2a** ($\leqslant$51%). To test the generality of ligation with a strong σ-donor, 20 mol% of the NHC 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene was used successfully in place of PR_3, giving **2a** in 94% yield.

Using favorable conditions identified from our reactivity survey involving **1a** (3 mol% AgOTf, 20 mol% Et_3P, THF, 70 °C), we sought to investigate the generality of the Ag-catalyzed hydrosilylation of aldehydes. Whereas *ortho*-tolualdehyde (**1b**) was reduced to **2b** in 94% yield (entry 4), lower conversions were obtained for the reduction of the more sterically hindered 2,6-dimethylbenzaldehyde **1c** (entry 6, 76%). Much faster reaction rates under more mild conditions were observed when 3 mol% AgOTf alone was employed as a catalyst for these transformations: however, significantly poorer selectivity for the desired hydrosilylation product **2** was obtained (entries 3 and 5). The aliphatic aldehydes **1d** and **1e** were also reduced more efficiently by use of Et_3P–AgOTf catalyst mixtures (entries 8 and 10) versus AgOTf alone (entries 7 and 9). Notably, when phosphine was employed in the reduction of **1d**, products derived from aldol condensation processes represented less than 3% of the consumed aldehyde.

In an effort to assess the chemoselectivity of Ag-mediated aldehyde hydrosilylation in the presence of either ketone or alkene functionalities, the reduction of 4-acetylbenzaldehyde (**1f**) and *trans*-cinnamaldehyde (**1g**) were examined. Whereas a mixture of products was obtained by using AgOTf as a catalyst (entries 11 and 13), both substrates were reduced cleanly by use of a Et_3P–AgOTf catalyst system, with 1,2 Si–H addition occurring exclusively at the aldehyde (entries 12 and 14).[10c] Notably, $(Ph_3PCuH)_6$ (Stryker's reagent) has also proven effective for the chemoselective hydrosilylation of aldehydes in the presence of ketones and alkenes.[4d] However, this Cu catalyst,[4e] like $(Ph_3P)_3RhCl$,[2e] has been shown to mediate the 1,4-conjugate hydrosilylation of α,β-unsaturated aldehydes, in contrast to the 1,2-addition brought about by the Et_3P–AgOTf catalyst system described herein in the hydrosilylation of **1g**.

While we are currently unable to comment as to whether the Ag-catalyzed hydrosilylation reactions detailed herein are homogeneous or heterogeneous in nature, the identification of $Me_2PhSiOTf$ as a by-product in these reactions suggests the possible intermediacy of AgH species. However, we do not view $Me_2PhSiOTf$ as being responsible for the observed reduction chemistry, given the distinct lack of hydrosilylation observed when Me_3SiOTf is employed in place of AgOTf, in the presence or absence of Et_3P (*vide supra*). Further experiments directed toward identifying the reactive Ag species present in such catalytic systems are currently underway in our laboratory.

In summary, this communication represents the first systematic evaluation of Ag-catalyzed carbonyl hydrosilylation. We have shown herein that AgOTf itself is able to catalyze aldehyde reductions under mild conditions, and that a catalyst system generated from AgOTf and an appropriate phosphine or NHC ligand is capable of mediating the chemoselective hydrosilylation of aromatic and aliphatic aldehydes. The recognition of such Ag-mediated reactivity highlights the need to consider the possible catalytic contributions of AgX species that may be present during metal-mediated hydrosilylation reactions.

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Notes and references

1 (*a*) J. F. Carpentier and V. Bette, *Curr. Org. Chem.*, 2002, **6**, 913; (*b*) I. Ojima, Z. Li and J. Zhu, in *Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, p. 1687.

2 Selected examples: (*a*) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440; (*b*) J. Yun and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 5640; (*c*) C. Eaborn, K. Odell and A. Pidcock, *J. Organomet. Chem.*, 1973, **63**, 93; (*d*) B. Tao and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 3892; (*e*) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugawa and Y. Nagai, *J. Organomet. Chem.*, 1975, **94**, 449.

3 W. S. Mahoney, D. M. Brestensky and J. M. Stryker, *J. Am. Chem. Soc.*, 1988, **110**, 291.

4 (*a*) B. H. Lipshutz and B. A. Frieman, *Angew. Chem., Int. Ed.*, 2005, **44**, 6345; (*b*) B. H. Lipshutz, C. C. Caires, P. Kuipers and W. Chrisman, *Org. Lett.*, 2003, **5**, 3085; (*c*) B. H. Lipshutz, K. Noson, W. Chrisman and A. Lower, *J. Am. Chem. Soc.*, 2003, **125**, 8779; (*d*) B. H. Lipshutz, W. Chrisman and K. Noson, *J. Organomet. Chem.*, 2001, **624**, 367; (*e*) B. H. Lipshutz, J. Keith, P. Papa and R. Vivian, *Tetrahedron Lett.*, 1998, **39**, 4627.

5 (*a*) S. Díez-González, N. M. Scott and S. P. Nolan, *Organometallics*, 2006, **25**, 2355; (*b*) S. Díez-González, H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *J. Org. Chem.*, 2005, **70**, 4784.

6 H. Ito, T. Yajima, J.-I. Tateiwa and A. Hosomi, *Chem. Commun.*, 2000, 981.

7 In a report pertaining to carbonyl hydrosilylations catalyzed by (pybox)$RhCl_3$–AgX, the ability of unligated AgX salts to mediate such transformations to a limited extent is mentioned briefly in a footnote; pybox–AgX mixtures did not exhibit any catalytic activity: H. Nishiyama, M. Kondo, T. Nakamura and K. Itoh, *Organometallics*, 1991, **10**, 500.

8 (*a*) C.-G. Yang, N. W. Reich, Z. Shi and C. He, *Org. Lett.*, 2005, **7**, 4553; (*b*) Y. Cui and C. He, *Angew. Chem., Int. Ed.*, 2004, **43**, 4210.

9 (*a*) X. Yao and C.-J. Li, *Org. Lett.*, 2005, **7**, 4395; (*b*) Y. Luo, Z. Li and C.-J. Li, *Org. Lett.*, 2005, **7**, 2675.

10 (*a*) Control experiments confirmed that 20 mol% Et_3P alone does not catalyze these transformations. Moreover, while the experiments reported herein were conducted using 99+% AgOTf (Aldrich), no change in catalytic behavior was noted for reactions employing 99.95+% AgOTf (Aldrich) that was found to contain only the following trace elements by ICP analysis (ppm): Na (13.5); Ca (1.6); B (0.8); Mg (0.3); Zn (0.1); Sb (0.1); (*b*) Et_3SiH and Ph_2SiH_2 proved less effective for this transformation†; (*c*) The identities of **2f** and **2g** were confirmed based on ^1H and ^{13}C NMR data.

11 M.-C. Brandys and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2002, **124**, 3946.